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POLYMER COMPOSITES CORROSIVE DEGRADATION: A COMPUTATIONAL SIMULATION

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ABSTRACT

A computational simulation of polymer composites corrosive durability is presented. The corrosive environment is assumed to manage the polymer composite degradation on a ply-by-ply basis. The degradation is correlated with a measured pH factor and is represented by voids, temperature and moisture which vary parabolically for voids and linearly for temperature and moisture through the laminate thickness. The simulation is performed by a computational composite mechanics computer code which includes micro, macro, combined stress failure and laminate theories. This accounts for starting the simulation from constitutive material properties and up to the laminate scale which exposes the laminate to the corrosive environment. Results obtained for one laminate indicate that the ply-by-ply degradation degrades the laminate to the last one or the last several plies. Results also demonstrate that the simulation is applicable to other polymer composite systems as well.

INTRODUCTION

Corrosion is a critical design requirement when composites are to be used in corrosive environments. These types of environments include pH factor, temperature and moisture and continuously degrade composites to the extent that they cannot sustain the load that they were initially designed to carry. Corrosion in metals has been extensively investigated [1]. Most of that information is for test methods and in other investigations the experimental investigation is emphasized [2,3].

The difficulty with the experimental investigation when using composite materials is that only a limited number of laminates can be investigated in limited corrosive environments. On the other hand, designs require lots of flexibility especially when the choice is about composite systems. In this regard, what is needed is a convenient way to manage composites to endure corrosive environments by computational simulation.

The objective of this article is to describe a convenient method that can be used to design polymer composites in corrosive environments. The method is a computational simulation method which correlates the pH of the corrosive environment to the resistance of the composite laminate. The resistance of the composite laminate is simulated by composite micro, macro and laminate theories. In this approach, the design for composite resistance to corrosive environments can start at the constituents and progress to the scale in which the laminate is exposed to the corrosive effects.

GENESIS OF PRESENT APPROACH

In this section, we describe the genesis of the proposed approach on how the approach to design/manage corrosion in composites was originated. The concept is based on establishing a relationship between the pH of the environment and the degradation of that environment on the laminate. The degradation of the laminate is in terms of pits which are formed in the polymer matrix in general. The corrosive environment may be also assumed to be a rise in use temperature as well as a level of humidity. The pH level is the degradation energy provided by the environment, whereas the void formation in the matrix in the laminate is the laminate measured degradation. The relation of pH to the voids formation then will be a solution to the problem. Discussions with the resident chemist led to values of pH of 14 which will dissolve the composite completely; whereas lower values less than 10 will corrode the polymer matrix substantially. This is only qualitative information.

The work reported in reference 4 shows test results that were conducted at pH values as follows: One series of tests was conducted in a pH environment of 4.7. The other identical series was conducted in an environment of 2.7. The 4.7 pH environment was the higher acidic concentration. The laminate degradation in terms of strength reduction was 33 percent of the series with the pH of 4.7 and 13 percent of the series with the pH of 2.7. If we now considered an 8-ply laminate, the 33 percent will result in a 3-ply degradation while the 13 percent will only degrade 1-ply. Now we have established an approximate time-in-dependent quantitative measure of ply corrosion degradation in a pH environment.

The next question is how to generalize the approximate quantitative information in order to predict corrosive composite degradation. Earlier we talked about the polymer matrix being corroded in the pH ranges that some experimental data existed. In composites polymer matrix degradation is simulated mostly by voids and by environmental effects. Therefore, the correlation between composite corrosion degradation due to pH environments is voids formed in the matrix on a ply-per-ply basis. That is the topmost ply which is exposed to the pH environment will corrode first, then the second, then the third and so on until the last one or several last plies corrode all at once. The concept is illustrated in figure 1. This kind of a behavior is reasonably represented by computation composite mechanics of the type programmed in ICAN (Integrated Composite Analyzer) [5]. A schematic of the ICAN composition is shown in figure 2. It is important to see the

progression of the multi-scale simulation as noted by the arrows. The details on how this can be done, type of results that are obtained, and how these lead to corrosion management are described in the following sections.

EVALUATION PROCEDURE

The evaluation procedure is as follows:

1. Assume that the pH will corrode the first exposed ply in the polymer matrix only.
2. Assume that the corrosion will pit the polymer matrix in a parabolic shape from “0” at the last ply to about 0.3 at the top ply (ply 8).
3. Assume that the ply is subjected to a linear varying temperature and moisture for “0” at the last ply (ply 1) to close the transition temperature about 270° and a moisture content of 4 percent at the top ply (ply 8).
4. Use these as input data to ICAN and get the results.
5. Degrade the plies one or more at a time from the first ply to the last ply or several last plies where the simulation shows failure by using a combined-stress failure-criterion. Each corroded ply has degraded to the point that cannot carry any more design load.
6. The simulation ends since the laminate has been completely degraded.

The above procedure is readily adaptable to computational composite mechanics computer codes, for example ICAN [5] which was used in the results obtained herein and described below.

RESULTS AND DISCUSSION

For the degradation simulation a $[0\pm45-90]_s$ AS graphite fiber/high-modulus high-strength polymer matrix was used. The results are summarized as follows: The void degradation is shown in figure 3—exposed ply 8 to ply 1. The effects of voids on the micro-mechanics geometric properties of the composite are illustrated in figure 4. It is observed in figure 3 that the voids affect each property through the equation of partial volumes. It is assumed that the maximum void degradation remains the same at the next ply as each degraded ply is removed. The temperature variation is shown in figure 5. The equations that describe how the thermal ply properties change are shown in figure 6. Note that the effects of the void enter as noted in the respective equation. It is also interesting to note that the maximum temperature in the first undegraded ply remains the same. The moisture degradation is shown in figure 7. The equations that describe the moisture effects in the composite are listed in figure 8 and the void effects are through the partial volume equations in figure 4. In this case also the exposed ply has the most moisture. The degradation effects on the ply properties are shown in figure 9 for the stiffness variations as each ply is corroded. The equations that describe how the moduli are affected by the changes in the different volume ratios are summarized in figure 10. Here it is seen that the longitudinal modulus (E_{l11}) degrades about 30 percent 130.9 to 89.6 GPa (from 19 to 13 mpsi). This degradation is due to the adjusted fiber volume ration from 0.60 to 0.42. Note the transverse and shear modulus degraded substantially from 82.7 to 2.76 GPa (1.2 to 0.4 mpsi) or about 70 percent reduction for the transverse modulus and from 0.6 to 0.2 mpsi or about 70 percent for the shear modulus. It is interesting to note that both of these degrade about the same since they are both matrix controlled quantities. It is also

interesting to note that managing of corrosion is limited to the first ply or portions thereof. The matrix in this ply may be selected with relatively small void formation due to corrosive environments. Or a sacrificial ply with corrosive resistance may be used as a first exposed ply.

The corresponding stress degradations are shown in figure 13. The structural analysis equations from which the stresses are calculated are summarized in figure 14 together with the combined stress function.

Note that the stresses in the first ply degrade substantially. It is interesting to look at the first ply combined stress failure criterion of -194. This indicates a measure of the total degradation in ply strength carrying capacity. Also, it is interesting to note the negative combined-stress failure criterion values in the other plies as the intact plies degrade. The positive value denotes that the corrosion degradation has not quite degraded that ply as yet. However, the last column indicates that the remaining three plies have all been degraded where they cannot carry any more load.

The ply strength degradation is shown in figure 11. The equations that describe how the strengths degrade with the changes in the different volume ratios are listed in figure 12.

Note that the longitudinal strength (S_{l11}) degrades from about 1.65 to 1.16 GPa (240 to 168 ksi), or about 30 percent, which is the same as that for the longitudinal modulus. This reduction is due to the adjusted fiber volume ratio. The remaining strengths which are matrix controlled quantities degrade to almost nothing. These other strengths are a measure that the corrosion has degraded the plies completely.

The u function in figure 14 includes both in plan displacements are curvatures. The symbol ω represents frequency. $[M]$, $[C]$, and $[K]$ represent mass, damping, and stiffness matrices respectively. $\{F(t)\}$ is a load vector. Applied stress is represented by σ and its corresponding strength by S . $[E]$ is the constitutive properties for composites matrix and $L(G)$ is a matrix operator which reduces the global displacements $\{u\}$ to the composite ply stresses $\{\sigma\}$.

The simulated corrosive degradation of the first ply in other fiber polymer matrix composites is summarized in table 1 where the fiber type is in the first left column, the moduli in the next four columns, followed by the uniaxial strengths, the ply stresses, combined-stress failure and the laminate strength in the last column. The constituent material properties from which the table was developed are resident in a databank in the ICAN computer code. It is interesting to note in the second last column in Table 1 the large values of the combined stress failure criterion which indicate that the first ply was gone long before that value was reached. This indicates that probably the time needs to be included in the simulation.

The results shown in the previous figures illustrate the essence of the corrosion procedure proposed for evaluating fiber composite degradation effects, which is by correlating the pH with void formation, temperature, and moisture. The equations summarized denote the inclusiveness of the simulation. As is seen in the results the corrosion affects the whole laminate through its thickness; however, the exposed surface gets the brunt of it. The results also show how the composite corrosion can be managed limiting that effect to a single ply or to a portion of that ply.

SUMMARY OF RESULTS

The salient results from and investigation on approximate treatment of designing/managing composites for enduring

corrosive environments are as follows: A formal approach for the design was described. The approach consists of relating the corrosive environment pH to the laminate's endurance. The approach is not time dependent. It is an instantaneous representation as the laminate degrades by the corrosive environment. The laminate degradation is represented by a void content with parabolic variation and by a linear temperature and moisture variation through the laminate thickness. Computational multi-scale composites mechanics from micro to macro, to laminate theories is used in the simulation. Results are presented for discarding ply-by-ply due to degradation for composite laminates. Results are also presented for the corrosive degradation of several polymer composites. Managing corrosion is limited to the selection of the matrix in the ply exposed to the corrosive environment.

REFERENCES

1. Anonymous: *2003 Annual Book of Standards: Wear and Erosion and Metal Corrosion*. sec. 3, vol. 03.02, ASTM International (2003).
2. I.A. Wooton, et al., Corrosion of Steel Reinforcement in Carbon Fiber Reinforced Polymer Wrapped Concrete Cylinders. *J. of Composites for Construction*, ASCE, pp. 339-347 (Nov 2003).
3. A. Jacob, Vinyl Esters Lead the Corrosion Challenge. *Reinforced Plastics*, pp. 32-35 (June 2003).
4. S.W. Hopkins, et al., Long Term Strain-Corrosion Behavior in RPM Sewer Pipes. *Composite Materials Testing and Design*, 14th Volume, ASTM STP 1436, C. E. Bakis, Ed, (2003).
5. P.L.N. Murthy and C.C. Chamis, *Integrated Composite Analyzer, (ICAN), Users and Programmers Manual*. NASA TP 2515, (1986).

Table 1. First-ply degradation due to corrosion for different composite systems (1 psi = 6.89 Pa).

| Composite system | Moduli, mpsi | | | Major strengths, ksi | | | | | | Stresses, ksi | | | Combined stress failure function | Laminate strength, ksi |
|------------------|--------------|-----------|-----------|------------------------------|------------|------------|------------|------------|------------|----------------|----------------|----------------|----------------------------------|------------------------|
| | E_{t11} | E_{t22} | G_{t12} | Poisson's ratio, ν_{t12} | S_{t11T} | S_{t11C} | S_{t22T} | S_{t22C} | S_{t12S} | σ_{t11} | σ_{t22} | σ_{t33} | | |
| 0.4B/EP | 24.4 | 4.48 | 1.66 | 0.287 | 252 | 0.84 | 0.08 | 0.20 | 0.06 | 1.8 | 0.85 | 0.019 | -113.7 | 14.8 |
| 0.5B/EP | 24.4 | 4.48 | 1.66 | 0.287 | 252 | 0.84 | 0.08 | 0.20 | 0.06 | 1.8 | 0.85 | 0.019 | -113.7 | 14.9 |
| 0.8B/EP | 24.4 | 4.48 | 1.66 | 0.287 | 252 | 0.84 | 0.08 | 0.20 | 0.06 | 1.8 | 0.85 | 0.019 | -113.7 | 14.9 |
| S-G/E | 5.3 | 0.44 | 0.16 | 0.287 | 151 | 0.84 | 0.08 | 0.20 | 0.06 | 2.9 | 1.5 | 0.10 | -339.1 | 4.4 |
| E-G/E | 4.4 | 0.44 | 0.16 | 0.287 | 151 | 0.84 | 0.08 | 0.20 | 0.06 | 3.0 | 1.5 | 0.13 | -376.8 | 3.9 |
| SiC/E | 26.0 | 0.45 | 0.16 | 0.324 | 210 | 0.84 | 0.08 | 0.20 | 0.06 | 1.6 | 0.86 | 0.23 | -115.8 | 15.8 |
| AS/E | 13.0 | 0.27 | 0.11 | 0.287 | 168 | 0.70 | 0.06 | 0.14 | 0.06 | 2.6 | 0.51 | 0.12 | -69.1 | 11.1 |
| Kev/E | 9.2 | 0.30 | 0.13 | 0.35 | 168 | 0.85 | 0.88 | 0.21 | 0.06 | 1.0 | 0.14 | ~0 | -291.2 | 9.5 |
| AS/E (Pristine) | 18.8 | 1.19 | 0.62 | 0.26 | 240 | 147 | 13.0 | 30.4 | 10.9 | 4.6 | 3.6 | 0.28 | 0.999 | 84.8 |

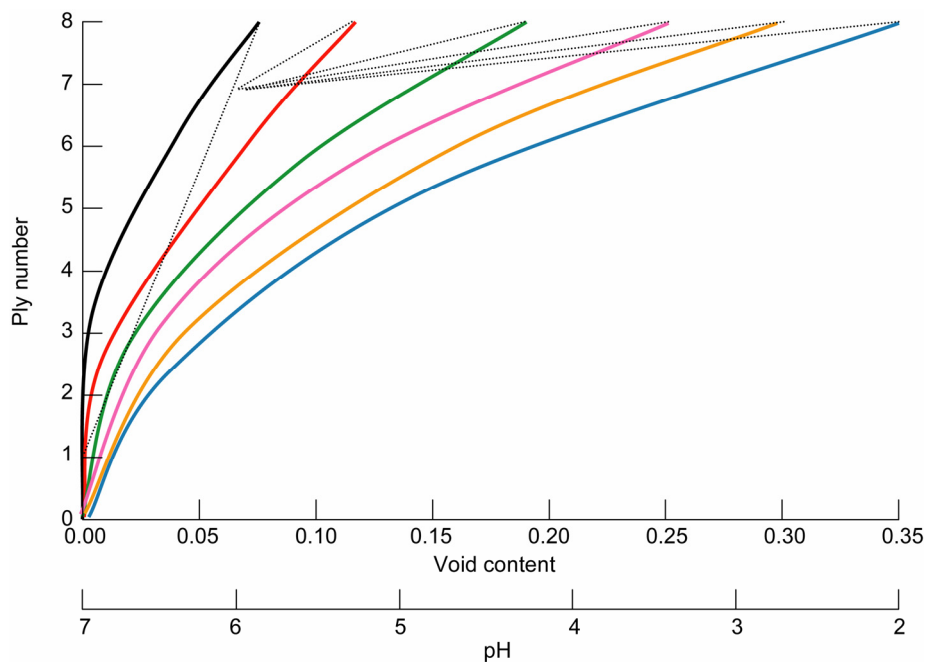


Figure 1.—Approximate pH correlation with ply degradation of AS/E [0/±45/90]_S composite (assuming parabolic voids variation through-the-thickness and linear temperature).

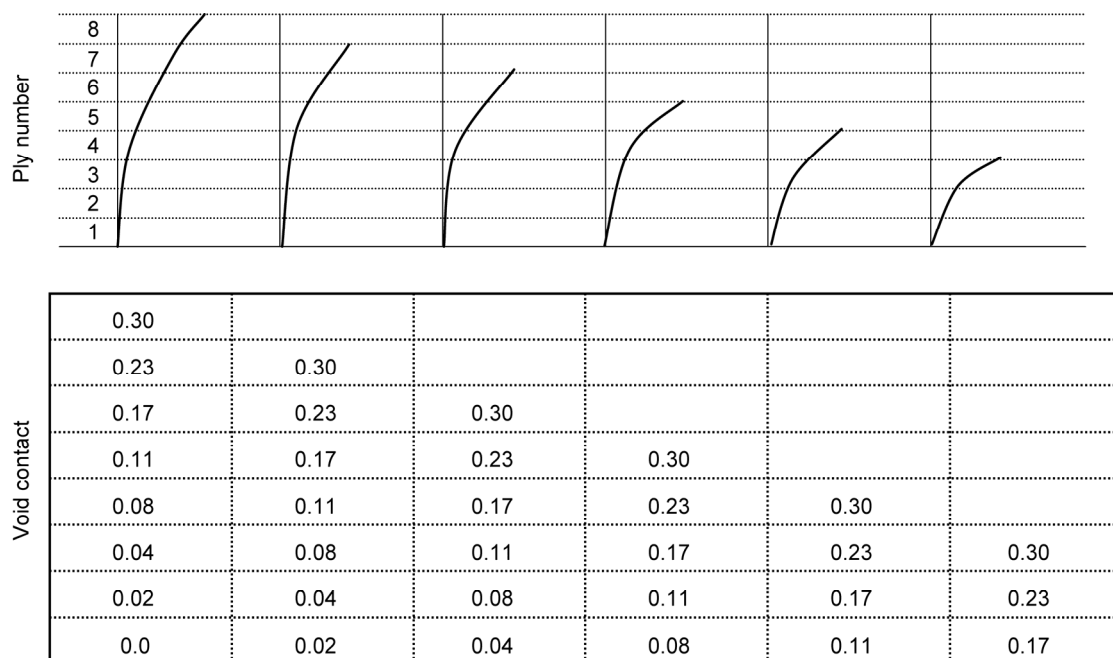
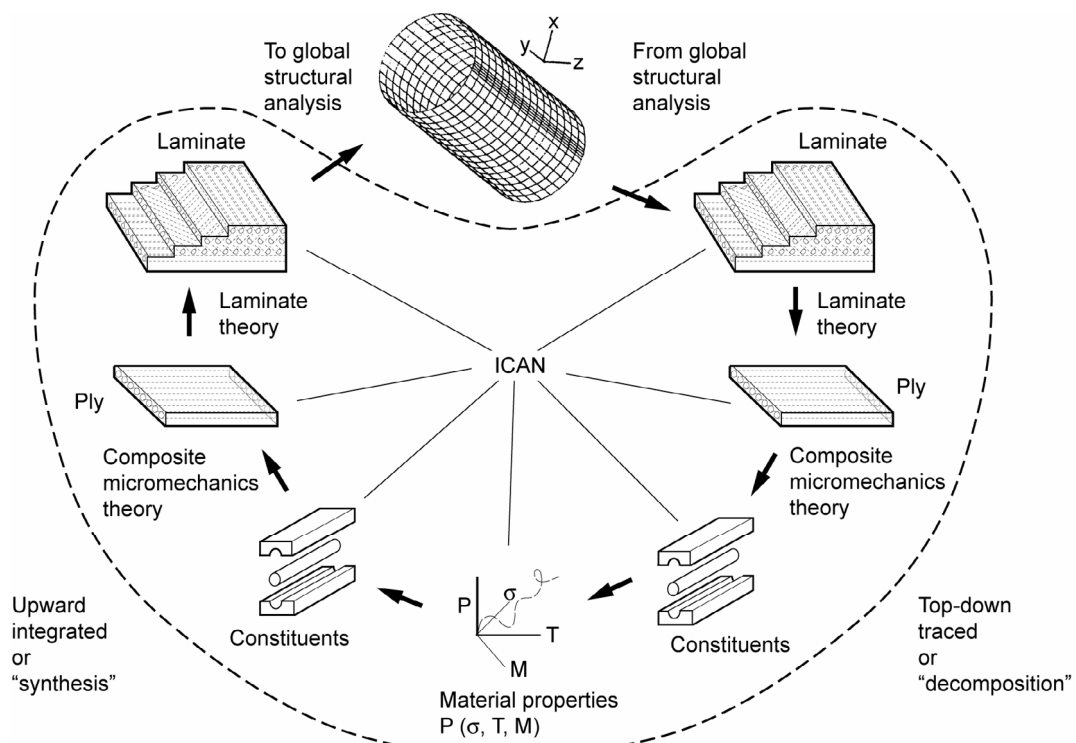


Figure 3.—Ply corrosion degradation $[0/\pm 45/90]_S$ AS/HMHS laminate. Corrosion simulated by parabolic void distribution, linear temperature and linear moisture through-the-thickness.

Partial volumes:

$$k_f + k_m + k_v = 1$$

Ply density:

$$\rho_\ell = k_f \rho_f + k_m \rho_m$$

Resin volume ratio:

$$k_m = (1 - k_v) / [1 + (\rho_m / \rho_f)(1/\lambda_m - 1)]$$

Fiber volume ratio:

$$k_f = (1 - k_v) / [1 + (\rho_f / \rho_m)(1/\lambda_f - 1)]$$

Weight ratios:

$$\lambda_f + \lambda_m = 1$$

Ply thickness (S.A.):

$$t_\ell = 1/2 N_f d_f \sqrt{\pi/k_f}$$

Interply thickness:

$$\delta_\ell = 1/2 \left[\sqrt{\pi/k_f} - 2 \right] d_f$$

Interfiber spacing (S.A.):

$$\delta_s = \delta_\ell$$

Contiguous fibers (S.A.):

$$k_f = \pi/4 \sim 0.785$$

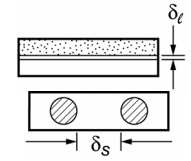
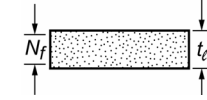
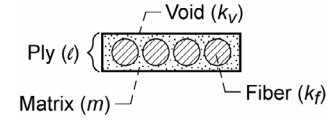


Figure 4.—Micromechanics and geometric relationships.

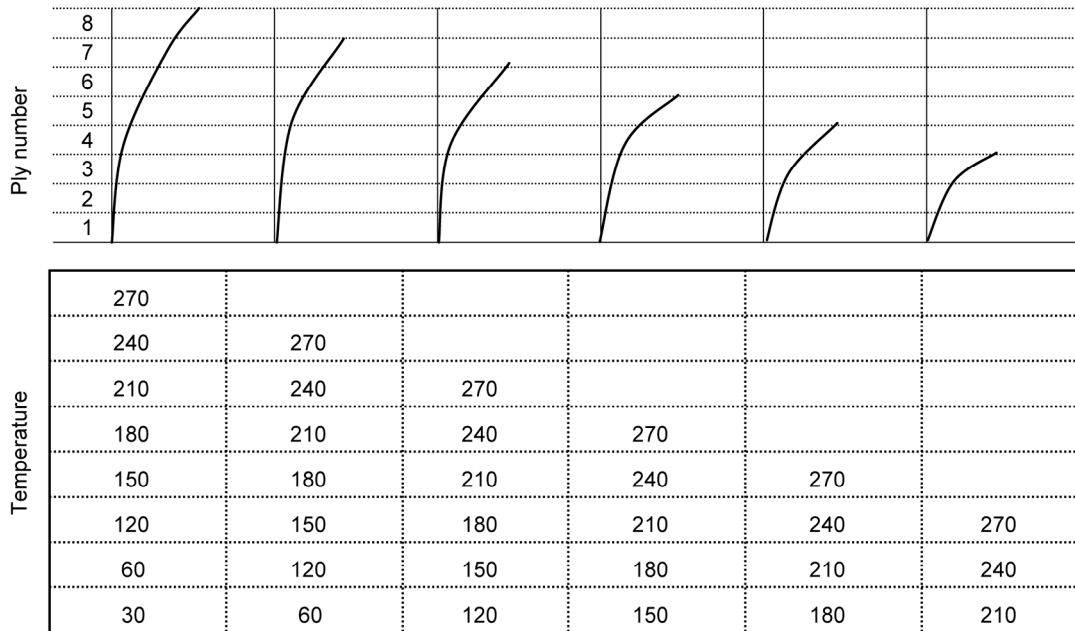


Figure 5.—Ply corrosion degradation $[0/\pm 45/90]_s$ AS/HMHS laminate. Corrosion simulated by parabolic void distribution, linear temperature and linear moisture through-the-thickness (voids-schematic; temperature table (1 °F = (5/9) °C)).

Heat capacity:

$$C_\ell = \frac{1}{\rho_\ell} (k_f \rho_f C_f + k_m \rho_m C_m)$$

Longitudinal conductivity:

$$K_{\ell 11} = k_f K_{f 11} + k_m K_m$$

Transverse conductivity:

$$K_{\ell 22} (1 - \sqrt{k_f}) K_m + \frac{K_m \sqrt{k_f}}{1 - \sqrt{k_f} (1 - K_m / K_{f 22})} = K_{\ell 33}$$

For voids:

$$K_m = (1 - \sqrt{k_v}) K_m + \frac{K_m \sqrt{k_v}}{1 - \sqrt{k_v} (1 - K_m / K_v)}$$

Longitudinal thermal expansion coefficient:

$$\alpha_{\ell 11} = \frac{k_f \alpha_{f 11} E_{f 11} + k_m \alpha_m E_m}{E_{\ell 11}}$$

Transverse thermal expansion coefficient:

$$\alpha_{\ell 22} = \alpha_{f 22} \sqrt{k_f} + (1 - \sqrt{k_f}) (1 + k_f v_m E_{f 11} / E_{\ell 11}) \alpha_m = \alpha_{\ell 33}$$

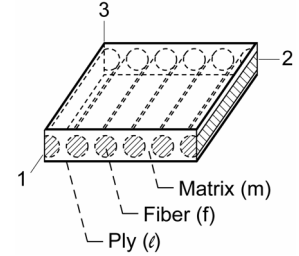


Figure 6.—Composite micromechanics, thermal properties.

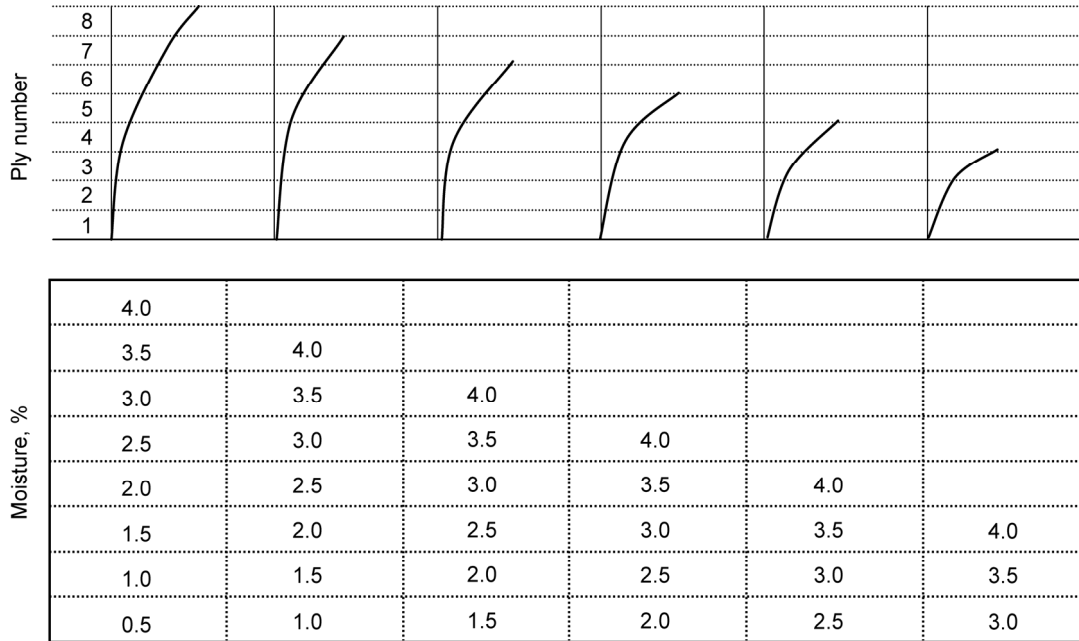


Figure 7.—Ply corrosion degradation $[0/\pm 45/90]_S$ AS/HMHS laminate. Corrosion simulated by parabolic void distribution, linear temperature and linear moisture through-the-thickness (voids-schematic; moisture table).

Longitudinal diffusivity:

$$D_{\ell 11} = (1 - k_f) D_m$$

Transverse diffusivity:

$$D_{\ell 22} = (1 - \sqrt{k_f}) D_m = D_{\ell 33}$$

Longitudinal moisture expansion coefficient

$$\beta_{\ell 11} = \beta_m (1 - k_f) E_m / E_{\ell 11}$$

Transverse moisture expansion coefficient:

$$\beta_{\ell 22} = \beta_m (1 - \sqrt{k_f}) \left[1 + \frac{\sqrt{k_f} (1 - \sqrt{k_f}) E_m}{\sqrt{k_f} E_{\ell 22} + (1 - \sqrt{k_f}) E_m} \right] = \beta_{\ell 33}$$

For incompressible matrix:

$$\beta_{\ell 11} = 0$$

$$\beta_{\ell 22} = \beta_m \rho_\ell / 2 \rho_m = \beta_{\ell 33}$$

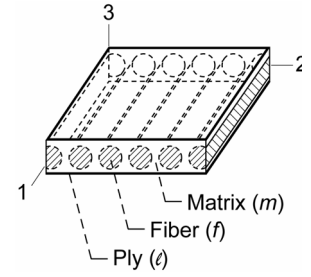
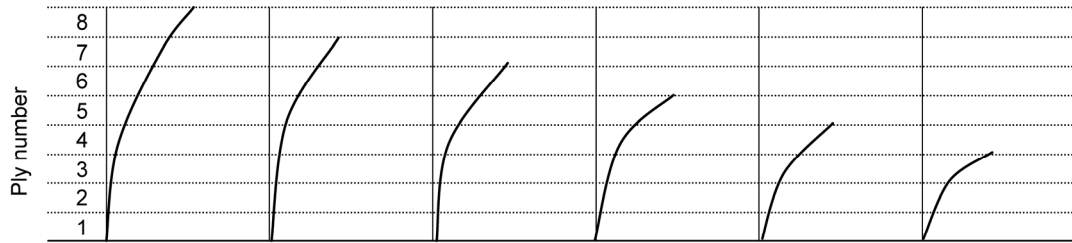


Figure 8.—Composite micromechanics, hygro properties.



| | | | | | | |
|---------------|-------|-------|-------|-------|-------|-------|
| $E_{\ell 11}$ | 13.00 | 13.00 | 13.00 | 13.00 | 13.00 | 13.00 |
| $E_{\ell 22}$ | 0.39 | 0.50 | 0.60 | 0.70 | 0.40 | 0.40 |
| $G_{\ell 12}$ | 0.16 | 0.20 | 0.30 | 0.30 | 0.20 | 0.20 |
| $V_{\ell 12}$ | 0.28 | 0.28 | 0.29 | 0.29 | 0.29 | 0.29 |

Figure 9.—Ply corrosion degradation $[0/\pm 45/90]_s$ AS/HMHS laminate. Corrosion simulated by parabolic void distribution, linear temperature and linear moisture through-the-thickness (first ply composite properties (1 psi = 6.89 Pa)).

Longitudinal modulus:

$$E_{\ell 11} = k_f E_{f11} + k_m E_m$$

Transverse modulus:

$$E_{\ell 22} = \frac{E_m}{1 - \sqrt{k_f} (1 - E_m / E_{f22})} = E_{\ell 33}$$

Shear modulus:

$$G_{\ell 12} = \frac{G_m}{1 - \sqrt{k_f} (1 - G_m / G_{f12})} = G_{\ell 13}$$

Shear modulus:

$$G_{\ell 23} = \frac{G_m}{1 - \sqrt{k_f} (1 - G_m / G_{f23})}$$

Poisson's ratio:

$$\nu_{\ell 12} = k_f \nu_{f12} + k_m \nu_m = \nu_{\ell 13}$$

Poisson's ratio:

$$\nu_{\ell 23} = \frac{E_{\ell 22}}{2G_{\ell 23}} - 1$$

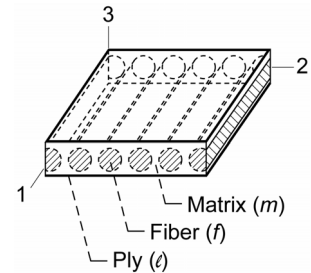
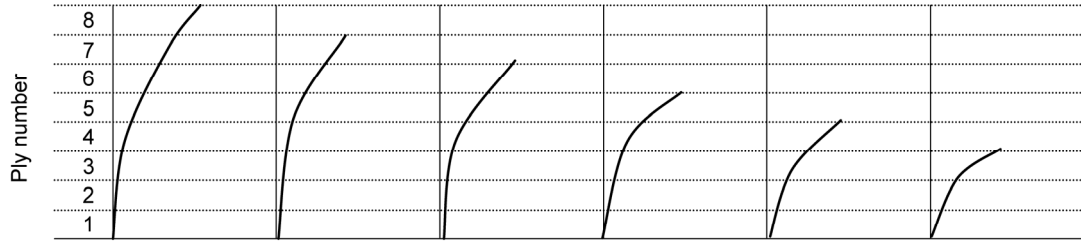


Figure 10.—Composite micromechanics and mechanical properties.



| | | | | | | |
|----------------|------|-----|-----|-----|-----|-----|
| $S_{\ell 11T}$ | 168 | 168 | 168 | 168 | 168 | 168 |
| $S_{\ell 11C}$ | 0.84 | 1.1 | 1.4 | 1.6 | 0.8 | 0.8 |
| $S_{\ell 22T}$ | 0.02 | 0.1 | 0.1 | 0.2 | 0.1 | 0.1 |
| $S_{\ell 22C}$ | 0.29 | 0.3 | 0.1 | 0.3 | 0.2 | 0.2 |
| $S_{\ell 12S}$ | 0.06 | 0.1 | 0.6 | 0.1 | 0.1 | 0.1 |

Figure 11.—Ply corrosion degradation $[0/\pm 45/90]_s$ AS/HMHS laminate. Corrosion simulated by parabolic void distribution, linear temperature and linear moisture through-the-thickness (first ply remaining strengths (1 psi = 6.89 Pa)).

1. Longitudinal tension:

$$S_{\ell 11T} \approx k_f S_{fT}$$

2. Longitudinal compression:

$$S_{\ell 11C} \approx k_f S_{fC}$$

Fiber compression:

$$S_{\ell 11C} \approx 10 S_{\ell 12S} + 2.5 S_{mT}$$

Delamination/shear:

$$S_{\ell 11C} \approx \frac{G_m}{1 - k_f \left(1 - \frac{G_m}{G_{f12}} \right)}$$

Microbuckling:

3. Transverse tension:

$$S_{\ell 22T} \approx \left[1 - \left(\sqrt{k_f} - k_f \right) \left(1 - E_m / E_{f22} \right) \right] S_{mT}$$

4. Transverse compression:

$$S_{\ell 22C} \approx \left[1 - \left(\sqrt{k_f} - k_f \right) \left(1 - E_m / E_{f22} \right) \right] S_{mC}$$

5. Intralaminar shear:

$$S_{\ell 12S} \approx \left[1 - \left(\sqrt{k_f} - k_f \right) \left(1 - G_m / G_{f12} \right) \right] S_{mS}$$

6. For voids:

$$S_m \approx \left\{ 1 - \left[4k_v / (1 - k_f) \pi \right]^{1/2} \right\} S_m$$

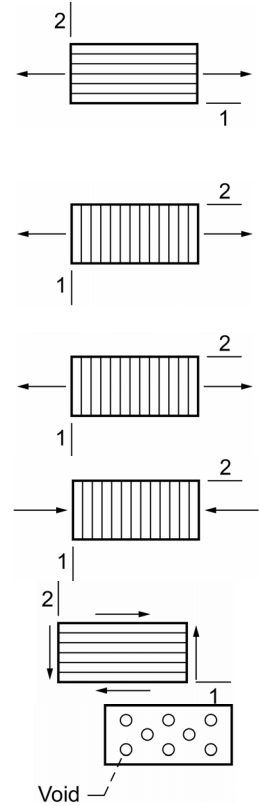


Figure 12.—Composite micromechanics, uniaxial strengths, in-plane.

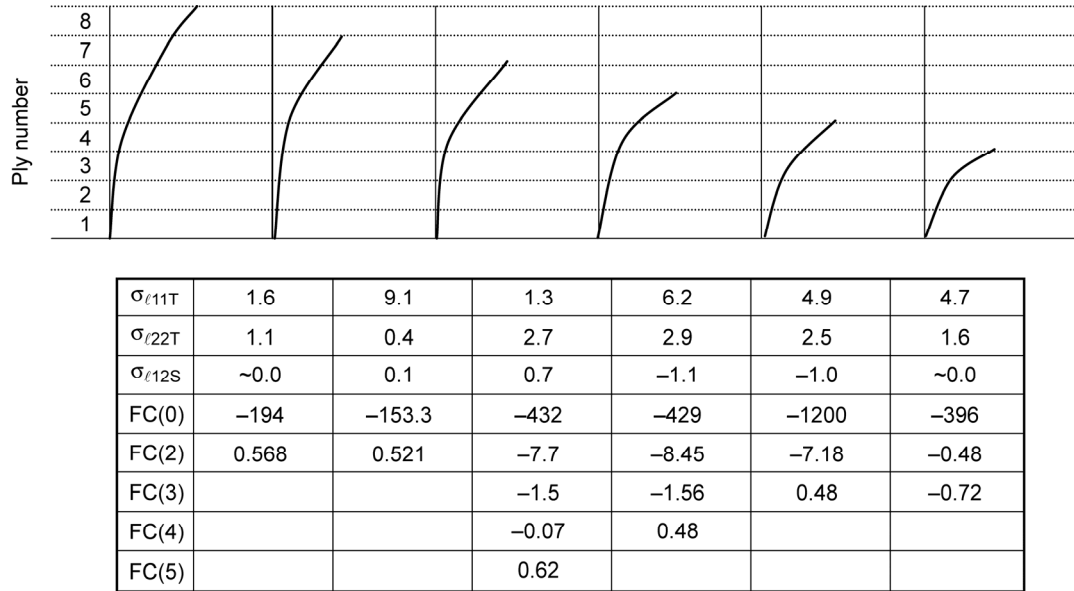


Figure 13.—Ply corrosion degradation [0/±45/90]S AS/HMHS laminate. Corrosion simulated by parabolic void distribution and linear temperature through-the-thickness (first ply stresses and combined stress failure-criterion (FC)); 1 psi = 6.89 Pa.

$$[M] \{\ddot{u}\} + [C] \{\dot{u}\} + [K] \{u\} = \{F(t)\}$$

$$\{\omega\} \leq \{\omega_a\}$$

$$\langle [K] - \omega^2 [M] \rangle \{u\} = 0 \rightarrow \{\omega\}$$

$$\{u\} \leq \{u_a\}$$

$$\{\sigma\} = [E]^{-1} [L(G)] \{u\} \leq \{S_a\}$$

$$F = 1 - \left[\left(\frac{\sigma_{l11\alpha}}{S_{l11\alpha}} \right)^2 + \left(\frac{\sigma_{l22\beta}}{S_{l22\beta}} \right)^2 - K_{l12} \left(\frac{\sigma_{l11\alpha}}{S_{l11\alpha}} \right) \left(\frac{\sigma_{l22\beta}}{S_{l22\beta}} \right) + \left(\frac{\sigma_{l12}}{S_{l12S}} \right)^2 \right]$$

$$F > 0 \text{ for no failure}$$

Figure 14.—Structural behavior/response governing equations.